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(54) Non-ionic surfactant with a low foaming power

(57) Non-ionic surfactant with a low foaming power, dilutable in water at any concentration, having general formula (II):

$$RO\text{-}(EO)_x\text{-}(PO)_y\text{-}(EO)_{x'}\text{-}(PO)_{y'}\text{-}H \qquad (II)$$

wherein R represents a linear or branched alkyl radical, containing from 9 to 15 carbon atoms, PO and EO respectively represent an oxypropylene and oxyethylene unit, x, x', y and y', the same or different, represent numbers of moles of said oxypropylene and oxyethylene units and range from 0.5 to 4.

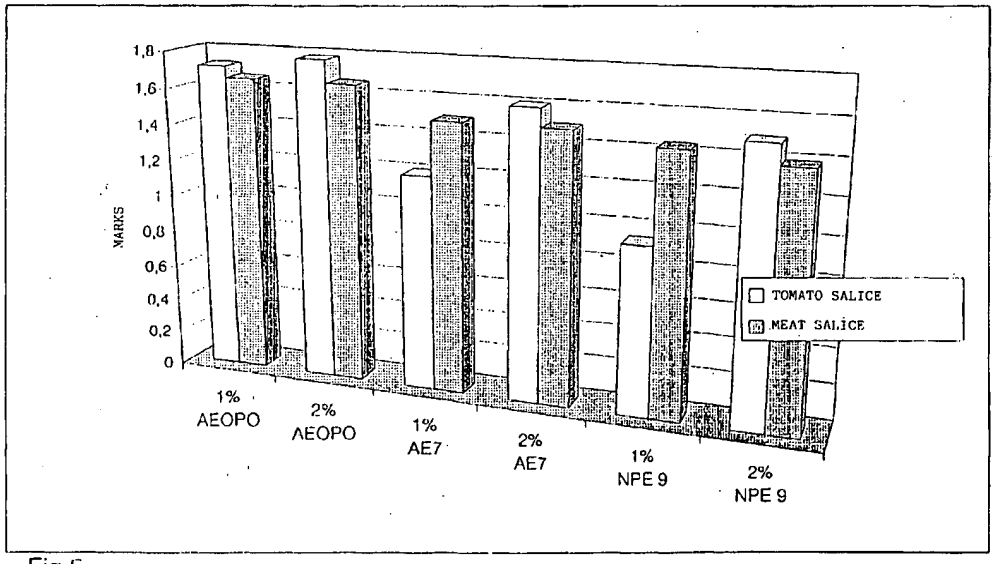

Fig.5

Description

[0001] The present invention relates to a non-ionic surfactant with a low foaming power.

[0002] More specifically, the present invention relates to a non-ionic surfactant for the formulation of detergent compositions with a low foaming power.

[0003] Non-ionic surfactants based on polymers of ethylene oxide are known in literature and their use in the field of detergency, as well as their characteristics and physico-chemical properties, are illustrated, for example, in Martin J. Schick "NON-IONIC SURFACTANTS, PHYSICAL CHEMISTRY" (1987).

[0004] European patent 882,785, moreover, describes a non-ionic surfactant which, although having a low foaming power, has detergency characteristics, and consists of a product having general formula (I):

$$RO\text{-}(EO)_x\text{-}(PO)_y\text{-}(EO)_z\text{-}H \qquad (I)$$

wherein R represents a linear or branched, C_{12}-C_{15} alkyl chain, EO and PO are an oxyethylene and oxypropylene unit respectively, and x, y and z the stoichiometric indexes equal to or higher than 1.

[0005] The surfactant having general formula (I) however, has a series of limitations, also listed in the European patent mentioned above, that make it substantially unsuitable for industrial use. In fact, the molecular weight of this product, for example, must not be higher than 1200 otherwise the detergent properties deteriorate. Or, it cannot be diluted in water in quantities of less than 50% by weight as with lower concentrations there are variations in the viscosity. The latter, moreover, must be less than 1000 cP otherwise there are problems in treating the solution. The succession of EO/PO oxides cannot be varied so as not to lose the detergent properties or the x, y and z indexes must remain within the limits established to avoid a reduction in the detergent properties, i.e. unsatisfactory rheological properties. These restrictions, and others specified in the test of the European patent, make the surfactant having general formula (I) of little interest from an industrial point of view.

[0006] With the objective of finding a non-ionic surfactant with a low foaming power which does not have the disadvantages of those of the known art, the Applicant has now discovered that by suitably alternating the succession of oxyethylene groups with oxypropylene groups, a product can be obtained which satisfies the required requisites, dilutable in water at any concentration and with higher detergent properties with respect to the traditional surfactants.

[0007] An object of the present invention therefore relates to a non-ionic surfactant with a low foaming power, dilutable in water at any concentration, having general formula (II).

$$RO\text{-}(EO)_x\text{-}(PO)_y\text{-}(EO)_{x'}\text{-}(PO)_{y'}\text{-}H \qquad (II)$$

wherein R represents a linear or branched alkyl radical, containing from 9 to 15 carbon atoms, preferably from 9 to 11 carbon atoms, PO and EO respectively represent an oxypropylene and oxyethylene unit, x, x', y and y', the same or different, represent the numbers of moles of said oxypropylene and oxyethylene units and range from 0.5 to 4.

[0008] The non-ionic surfactant having general formula (II) can be prepared with known techniques, for example by reacting an alcohol R-OH with propylene oxide and ethylene oxide, alternating blocks of the former with blocks of the latter, in the presence of a base catalyst selected from mixed oxides of magnesium-zinc, magnesium-tin, magnesium-titanium or magnesium-antimonium or from the hydroxdies of alkaline or earth-alkaline metals.

[0009] The alcohol R-OH is a known product, available on the market and sold by the Applicant under the tradenames of LIAL 11, LIAL 123, LIAL 125, LIAL 145, ALCHEM 11, ALCHEM 123, ALCHEM 125, ALCHEM 145, ISALCHEM 11, ISALCHEM 123, ISALCHEM 125, ISALCHEM 145 and NAFOL 1214.

[0010] For illustrative and non-limiting purposes, a non-ionic surfactant having general formula (II) was prepared wherein R is a C_{11} alkyl and the x and x' indexes are equal to 3, the index y is equal to 2 and the index y' is equal to 1.5.

[0011] 1720 grams of alcohol consisting of a mixture of linear and mono-branched alcohol with 11 carbon atoms are placed in an autoclave into which 1.2 grams of potassium hydroxide are charged. The autoclave is then heated to 100°C under vacuum to dehydrate the reaction mixture. The temperature was then brought to 135°C, pressurizing with nitrogen to 0.5 Kg/cm^2. The temperature is slowly brought to 150°C and 1320 grams of ethylene oxide are then slowly fed. At the end of the reaction of the ethylene oxide, when the pressure drop has been stabilized, 1160 grams of propylene oxide are fed.

[0012] This procedure is repeated, feeding a further 1320 grams of ethylene oxide and then 870 grams of propylene oxide.

[0013] At the end of the reaction the product was cooled to 80°C and neutralized up to pH 6 with acetic acid.

[0014] The product thus obtained, called AEOPO, was compared with traditional non-ionic surfactants. In particular,

the comparison was effected with an oxo-alcohol, with an alkyl chain having 11 carbon atoms, ethoxylated with 7 moles of ethylene oxide (AE/7) and with a nonylphenol ethoxylated with 9 moles of ethylene oxide (NPE 9).

[0015] The physico-chemical characteristics of the non-ionic surfactant of the present invention and traditional surfactants are indicated in table 1.

TABLE 1

		AEOPO	NPE 9	AE/7
Solidification temp	°C	<-10	3	10
Cloud point	°C	35	55	54
pH 5%		5.1	5.6	6
Density	g/cm^3	1.0021	1.0619	0.9980

Surface tension

[0016] Surfactants have the function of lowering the surface tension of aqueous solutions, favoring contact between components normally immiscible with each other, water and hydrophobic substances, and dissolving these substances inside their micelles.

[0017] Measurements carried out at different concentrations allowed the minimum surface tension value obtainable to be determined as well as the Critical Micellar Concentration (CMC) i.e. the concentration over which there is the formation of micelles. The results indicated in figure 1 show a surface tension value close to that of the ethoxylated alcohol with the same alkyl chain and lower than that of the ethoxylated nonylphenol. The CMC value, on the other hand, proves to be higher than that of other surfactants.

Wetting power

[0018] The determination of the wetting capacity of the surfactants was carried out according to the regulation ISO 8022 which comprises the measurement of the falling time of a cotton disc immersed in an aqueous solution of surfactant at different concentrations.

[0019] The results, indicated in figure 2, demonstrate that AEOPO has an excellent wetting power also with respect to other surfactants.

Foaming power

[0020] The verification of the foaming power was carried out using solutions at 2% by weight of surfactant. A mechanical system was used, consisting of a cylinder in which the foam was produced by a perforated piston driven by an electric motor. The system was regulated so as to stop after a preselected number of runs. The temperature was maintained at 20°C.

[0021] When the piston was stopped, the volume of foam, expressed in ml, which had formed above the layer of solution, was observed. The result of the test is illustrated in the graph of figure 3. For AEOPO two fundamental characteristics can be noted. A reduced foam level at the moment when the piston stops and a lower stability of the foam with respect to the comparative surfactants.

Rheological behaviour

[0022] The viscosity measurements were carried out at a constant temperature (25°C) with Cannon Fenske viscometers, also indicating the relative physical state or the possible formation of gel. The results are shown in figure 4.

[0023] On comparing the three surfactants, it can be observed that only AEOPO has a substantially constant viscosity, with limpid flowing solutions, whereas AE/7 has higher viscosities in the central zone which become rigid gel zones in the case of NPE 9.

Dirt Removal

[0024] In order to evaluate the efficiency of AEOPO, various dirt removal tests were carried out. Stains of dirty sample were deposited on an AISI 316 steel plate, using a measurement method which can produce a stain having a thickness of about 1 mm and with a surface of 20 cm^2.

[0025] The stains thus deposited were subjected to drying in an infrared-ray oven for one hour at 100°C. Two types of dirt were selected and precisely tomato sauce and roast meat sauce.

[0026] The test is carried out by depositing two drops of surfactant solution on the central part of the stain. After a period of 5 minutes the stains were washed with cold water at 20°C. The effectiveness of the surfactant was evaluated by observing the stains and the zones wetted by the surfactant. A mark was then given, corresponding to the degree of removal of the dirt, with respect to the non-treated zone of the stain.

No removal of dirt = 0;
partial removal of dirt = 1;
total removal of dirt = 2.

[0027] Tests were carried out for each surfactant with solutions of surfactant at 1% and 2% in demineralized water. The cycle of tests effected for each qualitative verification, included a number of 9 tests and the values indicated in figure 5 represent the average of the marks obtained.

Biodegradability

[0028] The biodegradability tests carried out on AEOPO gave positive results with respect to both primary and total biodegradability. Figure 6 shows the results obtained with the method described in the European regulation 82/242/CEE whereas the total biodegradability curves, shown in figure 7 and obtained with the MITI test, provide a further confirmation that AEOPO is easily biodegradable.

Claims

1. A non-ionic surfactant with a low foaming power, dilutable in water at any concentration, having general formula (II):

$$RO\text{-}(EO)_x\text{-}(PO)_y\text{-}(EO)_{x'}\text{-}(PO)_{y'}\text{-}H \qquad (II)$$

wherein R represents a linear or branched, alkyl radical containing from 9 to 15 carbon atoms, PO and EO respectively represent an oxypropylene and oxyethylene unit, x, x', y and y', the same or different, represent the numbers of moles of said oxypropylene and oxyethylene units and range from 0.5 to 4.

2. The non-ionic surfactant of claim 1, wherein indexes x and x' are equal to 3, index y is equal to 2 and index y' is equal to 1.5.

3. The use of the non-ionic surfactant of claim 1 in the preparation of water diluted detergent composition having low foaming power and high biodegradability.

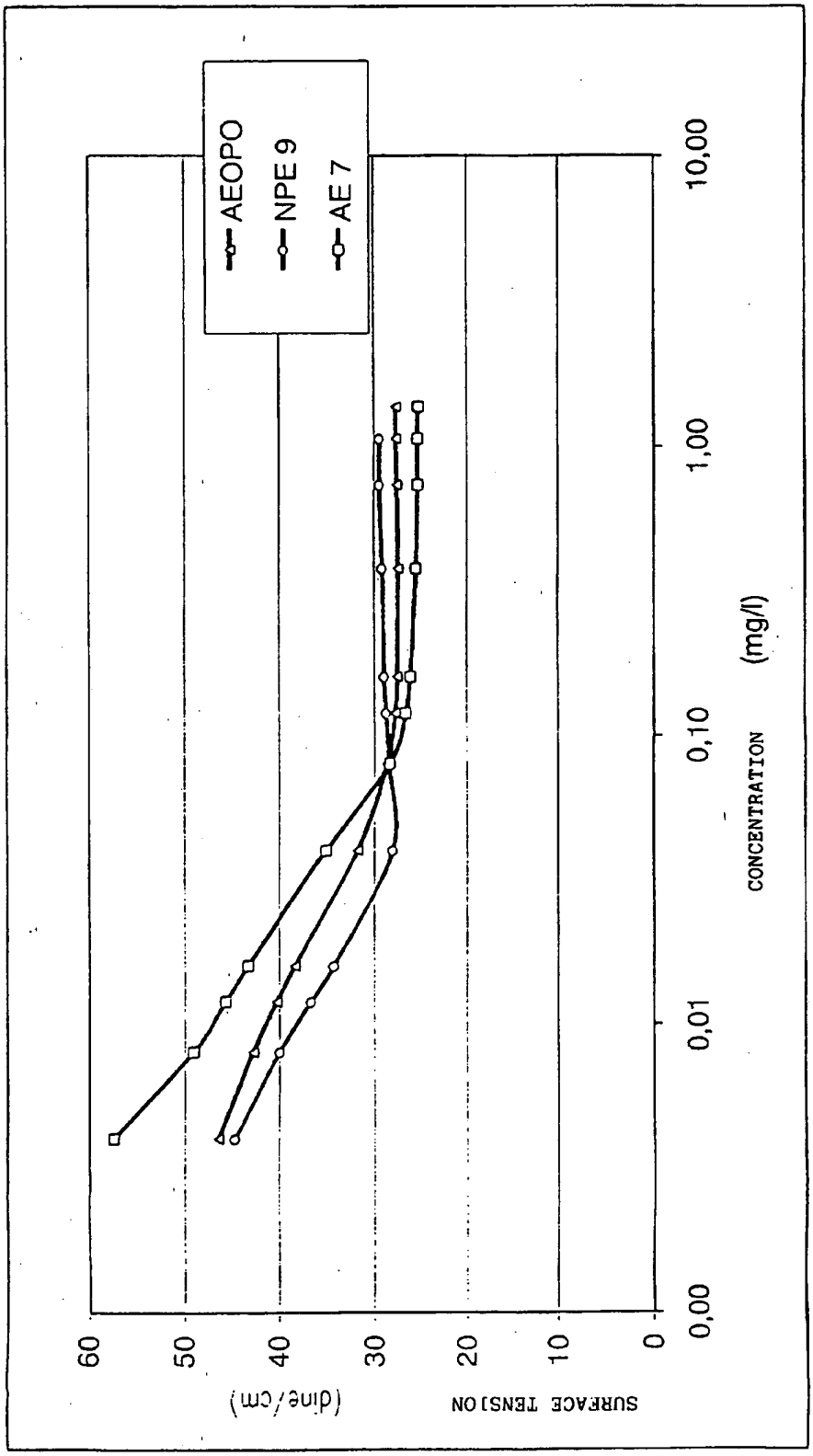
AEOPO
NPE 9
AE 7
SURFACE TENSION (dine/cm)
60
50
40
30
20
10
0
0,00
0,01
0,10
1,00
10,00
CONCENTRATION (mg/l)

Fig. 1

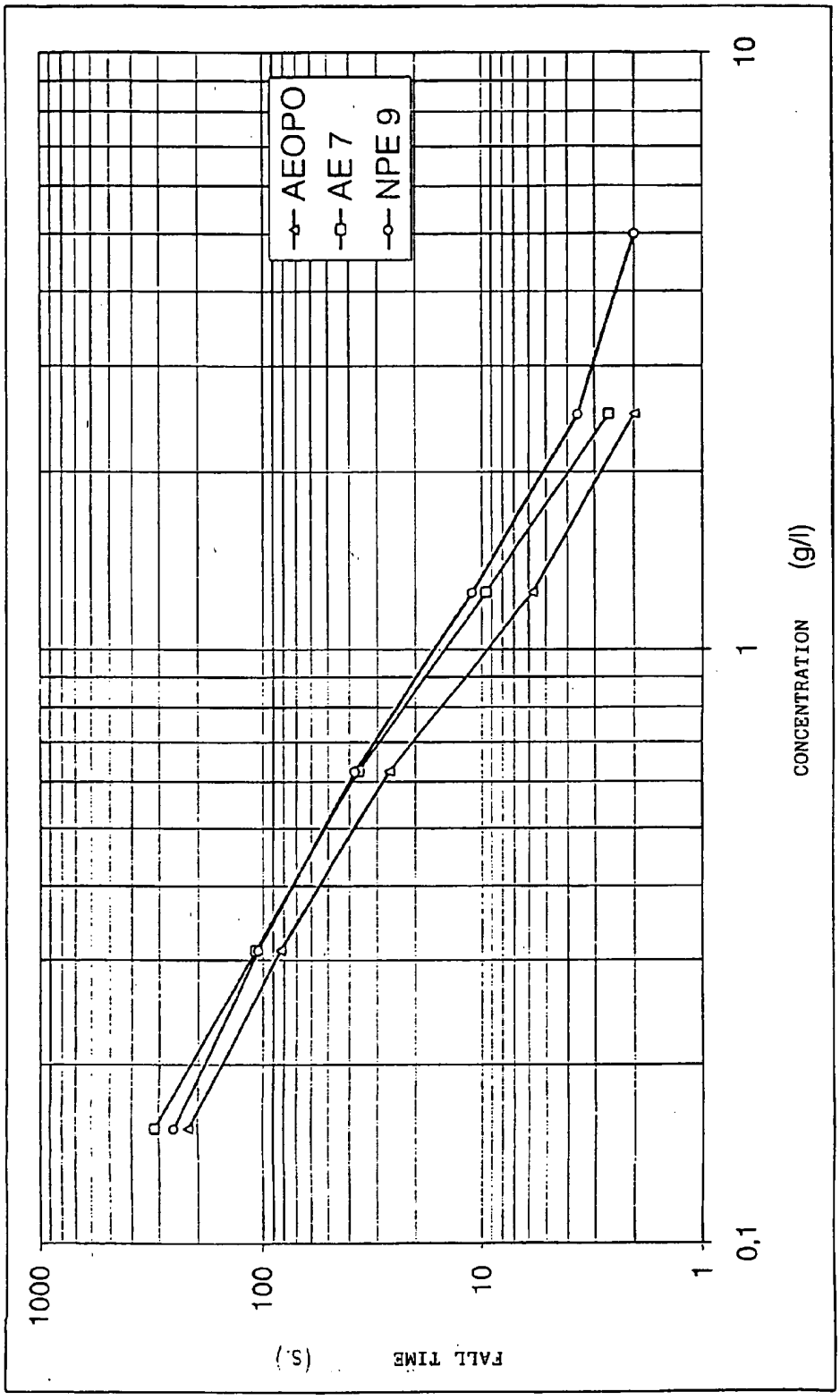
AEOPO
AE 7
NPE 9
10
1
0,1
CONCENTRATION (g/l)
1000
100
10
1
FALL TIME (S)

Fig.2

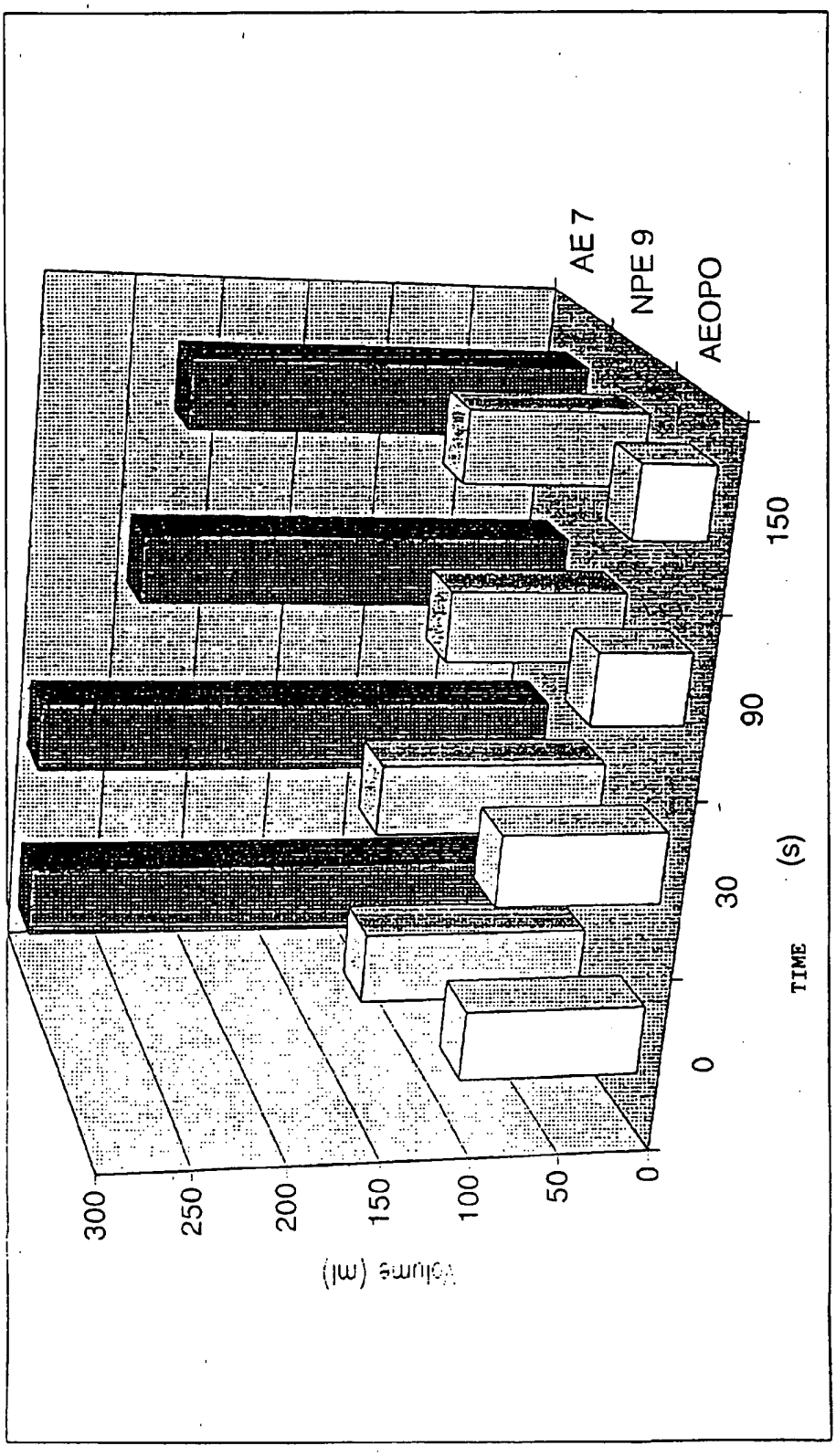

Fig.3

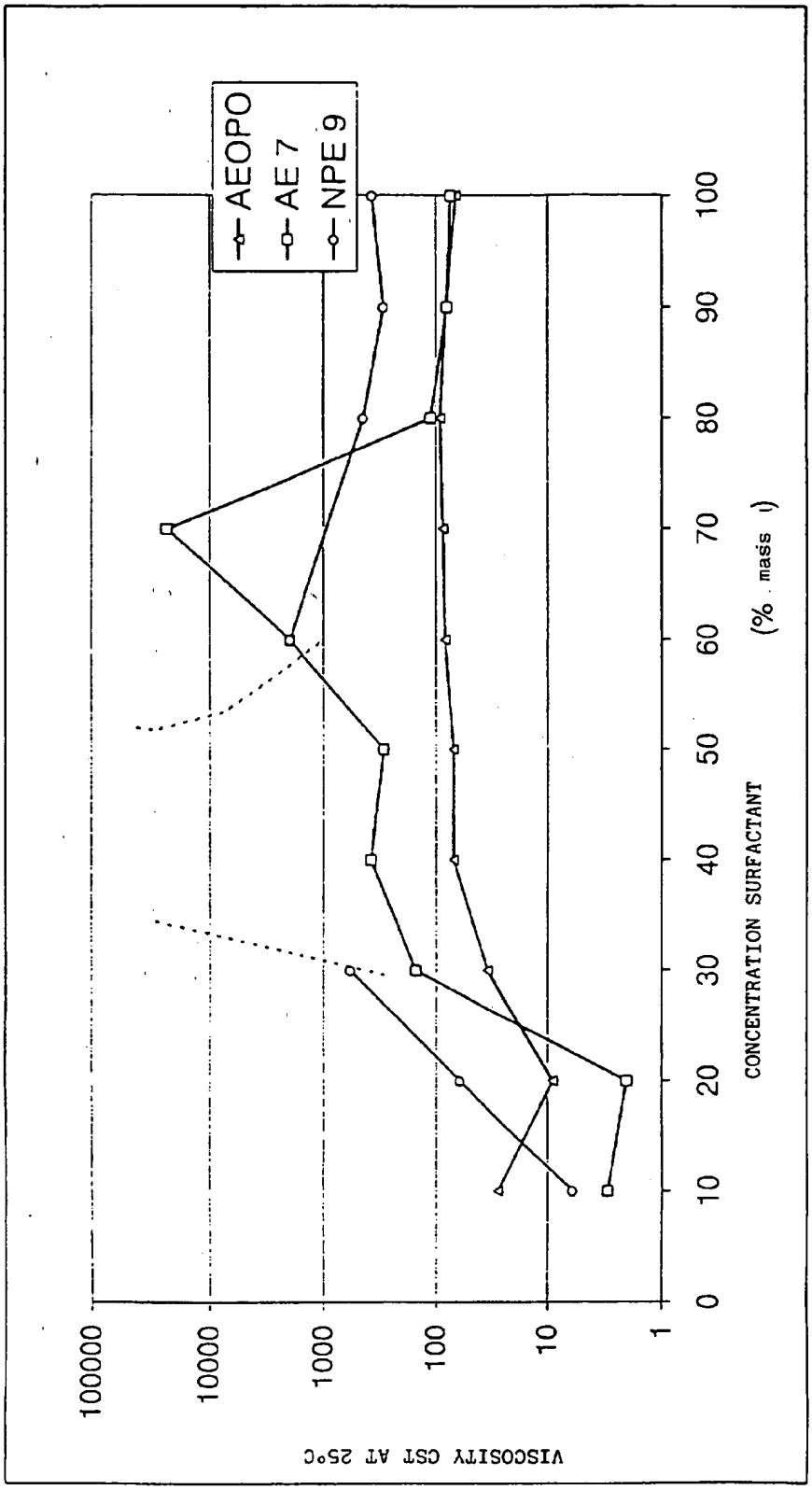
AEOPO
AE 7
NPE 9
VISCOSITY CST AT 25°C
100000
10000
1000
100
10
1
0
10
20
30
40
50
60
70
80
90
100
CONCENTRATION SURFACTANT (% mass)

Fig. 4

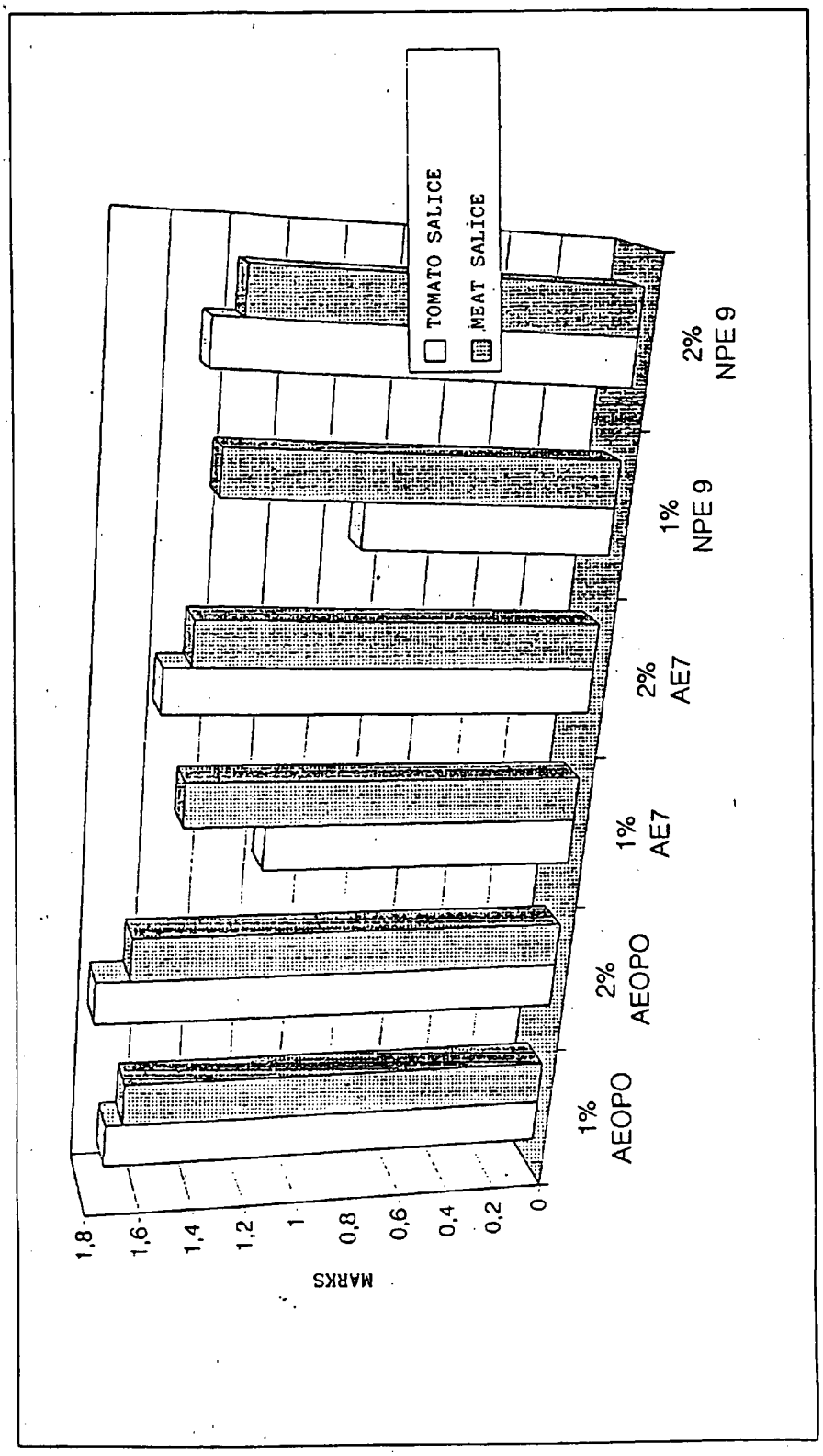

Fig.5

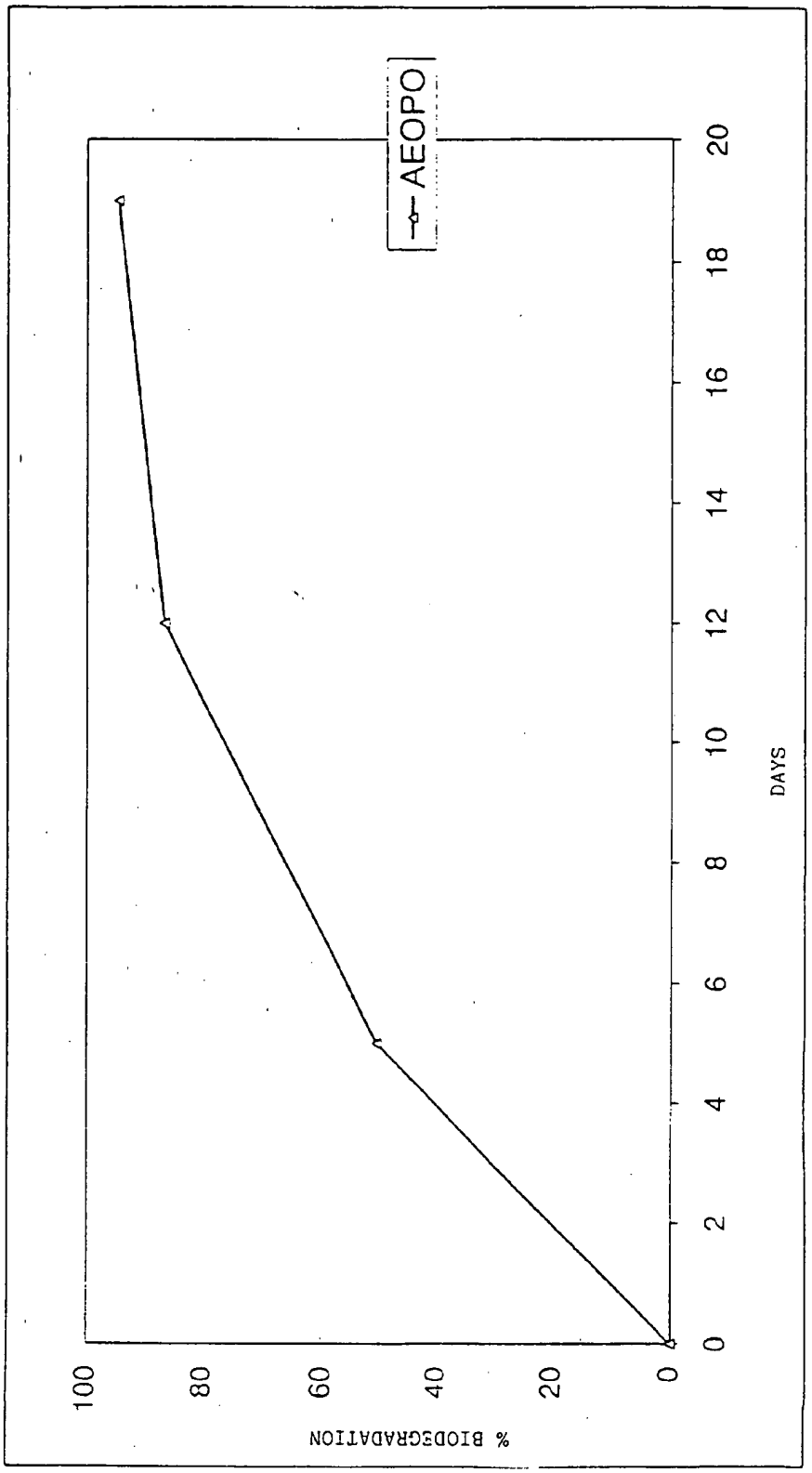
AEOPO
% BIODEGRADATION
0
20
40
60
80
100
DAYS
0
2
4
6
8
10
12
14
16
18
20

Fig.6


Standard
AEOPO
% BIODEGRADATION
0
10
20
30
40
50
60
70
80
90
TIME (DAYS)
0
5
10
15
20
25
30

Fig.7

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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 8136

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 110 503 A (COHEN ELLIOT) 5 May 1992 (1992-05-05) * column 3, line 2-4 * * column 4, line 28-45 * * column 6, line 14-52 *	1-3	C11D1/722 B01F17/42 B01F17/00
A	DE 197 03 083 A (HENKEL KGAA) 30 July 1998 (1998-07-30) * page 1, line 41-47 *	1-3	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C11D
B01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	7 July 2000	Pentek, E

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07-07-2000

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